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EQUILIBRIUM DISPLACEMENT IN A CHROMATOGRAPHIC REACTOR

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SUMMARY

The catalytic dehydrogenation of cyclohexane to benzene ($C_6H_{12} \rightleftharpoons C_6H_6 + 3H_2$) has been studied in a gas chromatographic reactor. An enhancement of product yield above equilibrium has been observed and direct evidence for equilibrium displacement obtained by the observation of a maximisation of yield at an optimum flow-rate. This optimisation is a result of the effects of flow-rate on peak broadening by longitudinal diffusion, an aspect which has been omitted in theoretical treatments of chromatographic reactors.

Further studies with a longer reactor showed considerably greater yields but no maximisation. In this case three product peaks were obtained. However, it has been shown that all three peaks are in fact benzene and not benzene pre-cursors as previous workers have assumed. A study of the decomposition of such precursors, *e.g.* cyclohexane and cyclohexa-1,3-diene has been made and the mechanistic and chromatographic implications of this have been discussed.

INTRODUCTION

The yields of useful products from conventional flow reactions are ultimately limited either by the value of the equilibrium constant or by the consumption of primary products by secondary reactions. By combining in one reactor both catalytic and chromatographic functions and by pulsing the reactants both of these limitations can be removed. The back reaction can be minimised by chromatographically separating the products from each other, while secondary reactions may be reduced by retaining the primary product on the column relative to the reactant pulse.

Several experimental and theoretical studies of equilibrium displacement on small bore columns have been made¹⁻⁸, but the evidence of displacement is equivocal. The comparison between experimental yield and estimated equilibrium yield involves many assumptions, and in addition there are unusual and unexplained features in some of the reported experiments (*e.g.* the effect of the ratio of pulse size to column length on conversion)².

The careful study of the dehydrogenation of cyclohexane to benzene reported here provides more direct evidence for displacement, and is in accord with the theoretical predictions of a maximisation by Gore⁸ who used digital methods to treat

the effects of finite equilibrium rates on the extent of displacement. However, we believe the maximisation is the result of a chromatographic aspect which Gore specifically did not include in his model.

EXPERIMENTAL

The catalyst chromatographic bed used was 0.72% platinum on silica (chromatography grade; Woelm, Eschwege, 6.F.R.) and was prepared by the "ammine complex" method of Dorling and Moss⁹. The BET surface area was 525 m² g⁻¹ and the platinum crystalite size was *ca.* 1.5 nm.

The apparatus was home-made, based on a Pye Unicam "Research" chromatograph. Detection was by a Taylor-Servomex micro-katharometer and the peak areas were measured with a Hewlett-Packard Model 3373B electronic integrator.

The reactor was constructed from 4 mm diameter glass tubing and consisted of two sections: the catalyst section contained the platinum/silica catalyst and was varied in length from 0.06 to 1.0 m; the analytical section was 0.30 m and was packed with silica (Woelm).

The temperature of the two sections could be varied independently; that of the catalyst section, requiring precise control, was achieved to better than $\pm 0.5^\circ\text{C}$ by using an air thermostat linked to a Mini-Therm proportional controller as a temperature trimmer. The temperature of the analytical section was controlled by the Pye oven controller. Helium was used as carrier gas after removed of impurities by passage through a one metre tube of silica. It was found that the degree of conversion was very sensitive to impurities in the carrier gas and to impurities inadvertently admitted to the system. To prevent this, and also to reduce the build up of carbonaceous matter on the catalyst, a stream of helium was maintained through the column at all times. Even with this precaution it was found necessary to reactivate the catalyst at intervals by further reduction in hydrogen.

The reactant was pulsed into the reactor using a microlitre syringe or a gas sampling valve (Pye-Unicam).

In some experiments it was necessary to investigate the integrity of the emergent chromatographic peak. This was done by collecting the emergent peak in a capillary tube packed with glass wool, extracting the sample with toluene and injecting into a Perkin-Elmer Model F.17 analytical chromatograph with a flame-ionization detector.

RESULTS AND DISCUSSION

The degree of conversion, α

The degree of conversion, α , of cyclohexane to benzene was usually determined from the benzene and cyclohexane peak areas after sensitivity corrections had been made,

$$\alpha = \frac{\text{benzene peak area}}{\Sigma \text{benzene} + \text{cyclohexane}} \quad (1)$$

Although a hydrogen peak (negative) was usually observed its calibration and measurement was more prone to error. A check on carbon balance was made routinely by

adding *n*-pentane as an internal standard (*n*-pentane is inert under the present conditions) to the cyclohexane. This showed that all the cyclohexane lost appeared as benzene (to within 2%) and thus allowed us to use eqn. 1 for α determination and hence dispense with the need for the internal standard for most experiments.

Theoretical equilibrium yields

Both the presence of inert gas (helium) and pressure affect the equilibrium yields. It can be shown for the cyclohexane dehydrogenation reaction that

$$\frac{K_p (1 - \alpha)}{27p^3} = \frac{\alpha^2}{\left\{ 3\alpha + 1 + \frac{n_{\text{He}}}{n_0} \right\}^3} \quad (2)$$

where K_p is the equilibrium constant, p is the total pressure and n_{He}/n_0 is the ratio of the number of moles of helium to number of moles of benzene in the pulse.

K_p was calculated from the free energy functions, for benzene, cyclohexane and hydrogen at the relevant temperature; the pressure p was measured at the reactor inlet, (the correction for pressure drop in the reactor was trivial); the ratio n_{He}/n_0 was calculated from the width of the cyclohexane peak at half peak height corrected for band broadening in the analytical column, together with the flow-rate and pressure to determine n_{He} . This gives an average value of n_{He}/n_0 in the reactor. Equilibrium values of α (α_{eq}) were obtained by graphical and numerical solutions of eqn. 2. It is of interest to note that the effect of the inert gas can give quite high values of α even when the equilibrium constant is very low (e.g. K_p at 160°C is $3.1 \cdot 10^{-6} \text{ atm}^3$ but α is still 0.098).

Effects of temperature and flow-rate on the theoretical and experimental value of α

A typical chromatogram from a 1- μl cyclohexane pulse is shown in Fig. 1a.

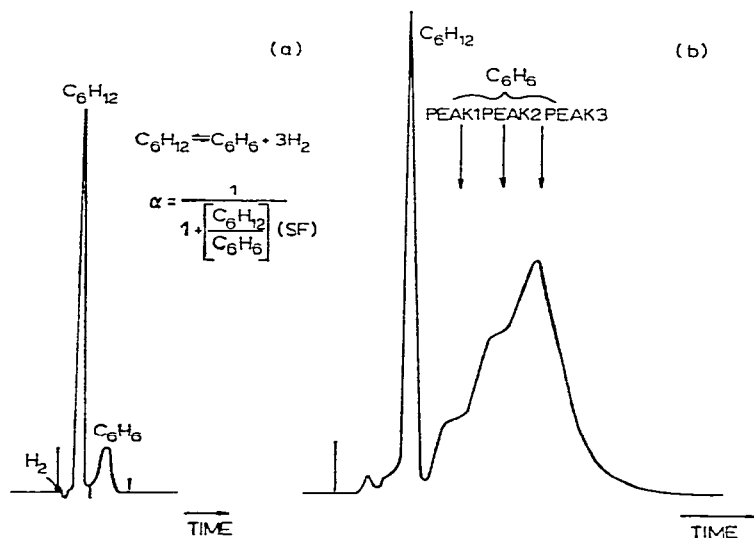


Fig. 1. Typical chromatograms from the chromatographic 0.06-m (a) and 1.0-m (b) reactors.

Values of the degree of conversion (α) at 160, 180, 200 and 240°C calculated from such chromatograms were measured with a standard deviation of less than 2%. The results for the short bed reactor (0.06 m) are shown in Fig. 2 together with the equilibrium values at 160, 180 and 200°C calculated from eqn. 2.

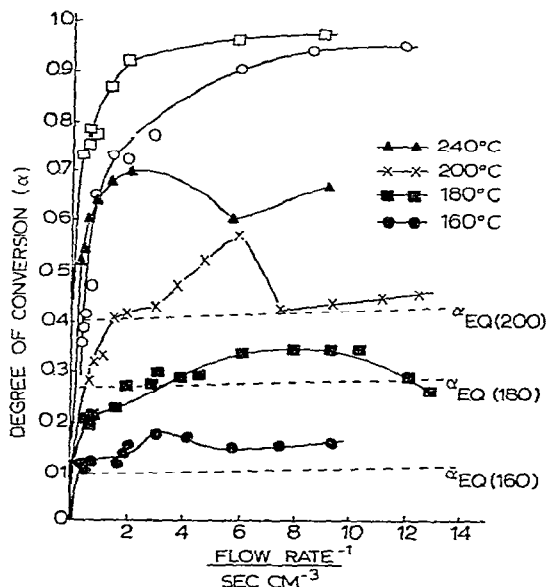


Fig. 2. Degree of conversion (α) and α_{EQ} as a function of flow-rate and temperature. Open symbols: results from the 1.0-m reactor; closed symbols: results from the 0.06-m reactor. Note: the 180, 200 and 240°C curves (0.06-m reactor) have been displaced upwards by 0.1 unit of α for clarity.

There are two features of interest, the occurrence of a maximisation of α at certain flow-rates and the fact that this maximum is well above (*ca.* 50%) the equilibrium conversion. Both are indicative of the displacement of the equilibrium by the chromatographic process and it appears to us that the occurrence of the maximum at an optimum flow-rate provides unequivocal proof of such a displacement since no theoretical estimates and experimental results are being compared and we can see no way of explaining the maximum in terms of equilibrium conditions on the column.

We are undertaking a full quantitative analysis of the system by solving the differential equations involving flow and reaction using numerical methods but the effects of flow-rate on α can be discussed semiquantitatively as follows: The displacement of equilibrium by reduction of the back reaction will be favoured by minimising the overlap between the product benzene and hydrogen peaks. Thus the effect of flow-rate on the displacement is essentially a chromatographic effect until the flow-rates become so large that short residence times coupled with finite reaction rates reduce conversions even to below the equilibrium value. The spatial separation between the band centres of the benzene and hydrogen peaks, Δz , is given by eqn. 3 and will be independent of flow-rate to a first approximation.

$$\Delta z = L[1 - k_{H_2}/k_B] \quad (3)$$

where L is the column length, and k_{H_2} and k_{B} are the partition coefficients for hydrogen and benzene, respectively.

The width of the bands, Δx , will increase as a result of axial diffusion and will be given by eqn. 4

$$\Delta x = \sqrt{\sigma^2 + \frac{2DL}{uk_{\text{H}_2}}} \quad (4)$$

where σ is the initial band width, u is the linear velocity of the carrier gas and D the diffusion coefficient for the relevant component in the carrier gas. Because the pressure increases with increasing flow-rate the diffusion coefficient will decrease somewhat with increasing flow-rate. The relationship between D and the flow-rate is of the form $D = A(1 + Cu)^{-1}$, where A and C are constants. The value of σ will increase with increasing flow-rate. Adding all these functions together gives eqn. 5 where B is a constant.

$$\Delta x = \sqrt{Bu + \frac{AL}{u(1 + Cu)k_{\text{H}_2}}} \quad (5)$$

Experimentally we find that Δx is approximately proportional to $u^{-\frac{1}{2}}$ for the cyclohexane peak indicating that the effect of diffusion and initial band widths are small compared with axial diffusion in the reactor, *i.e.* $\Delta x \propto u^{-\frac{1}{2}}$. The overlap between the benzene and hydrogen peaks will be a function of the separation of the band centres Δz and the peak widths Δx . Since Δz is independent of flow-rate the overlap will only show a flow-rate dependence because of its effects on peak width Δx . An increase in flow-rate results in a reduction in Δx , less overlap and hence more displacement of the equilibrium.

Of course at very high flow-rates two kinetic features become important. Firstly at high flow-rates the rates of adsorption and desorption will be too low for phase equilibria to occur and secondly the rates of the dehydrogenation steps will become too low for the full benefit of displacement to accrue. The occurrence of these two kinetic limitations may explain the occurrence of a knee on the curves shown in Fig. 2 rather than a maximum dropping without interruption to zero conversion.

It is of interest to note that the maximum observed arises because of axial diffusion. Although a similar maximum has been predicted by Gore⁸ who modelled such systems using an analogue computer we are unable to discover the physical basis of the maximum in Gore's work since he specifically ignores the effects of axial diffusion.

Effect of the length of the reactor bed

As shown in Fig. 2 the degrees of conversion are markedly increased in the 1-m bed compared with the 0.06-m bed, values of α of 0.9 to 1 being obtained at flow-rates below 10 ml min⁻¹. Such an increase in displacement is expected because the peak separation Δz increases with L while the peak broadening Δx increases only as $L^{\frac{1}{2}}$. Thus in the longer bed lengths peak overlap is reduced to zero at the reactor outlet even at very slow flow-rates. The effects of peak broadening which result in a

maximum in α in the small reactor are now insignificant compared with the peak separation. The fall in α at high flow-rate is again a result of the two kinetic effects.

The complex nature of the benzene peak in the long reactor

A typical chromatogram from the reactor shown in Fig. 1b is seen to have three poorly resolved peaks following the cyclohexane peak. We, like other workers, thought that these were benzene and its two precursors, cyclohexane and cyclohexa-1,3-diene. However, when the three peaks were collected and reanalysed on the analytical chromatograph we found that only one peak, that of benzene, was observed under conditions where the four C_6 hydrocarbons were readily resolved. Thus the three peaks emerging from the 1-m chromatographic reactor are all due to benzene.

Our tentative explanation of this unusual phenomenon is in terms of three processes leading to benzene at three different rates. These could involve three different types of catalytic site or three different routes although the occurrence of two peaks in addition to benzene does suggest that the two benzene precursors, cyclohexene and cyclohexa-1,3-diene are involved. The retention time of pure benzene injected into the reactor corresponds to the last and major peak. The route to this peak must be fastest so that the benzene is formed early in the bed and then behaves chromatographically like an injected pulse of benzene. The first peak after cyclohexane is due to benzene formed by the slowest process while the mid peak is formed at an intermediate rate. In summary we believe that three distinct kinetic processes lead to the formation of three separate bands of benzene at three different locations in the reactor and that these three bands are eluted as three distinct but poorly resolved peaks.

We have undertaken a careful study of the dehydrogenation of cyclohexene and cyclohexa-1,3-diene in the same reactors and have found these to react much more rapidly than cyclohexane (even at temperatures as low as 50°C) and to result in disproportionation. Thus in the case of cyclohexene, cyclohexane and benzene are formed and at sufficiently slow rates the ratio is exactly 2:1 as expected from the stoichiometry of the reaction



In the case of the diene, cyclohexane, cyclohexene and benzene are formed. At sufficiently long retention times no cyclohexene is observed and the ratio of cyclohexane to benzene is now 1:2 as expected from the reaction



The free energy changes for these reactions are so large (>150 kJ/mol) that they are the only reactions that need to be considered. Tentatively we suggest that the three peaks involve three reaction pathways: (1) direct rapid conversion of cyclohexane to benzene and hydrogen (peak 3), (2) conversion to cyclohexene followed by reaction a and then further dehydrogenation of cyclohexane to benzene (peak 1), (3) conversion to cyclohexadiene followed by reaction b, again followed by cyclohexane dehydrogenation to benzene (peak 2).

The results in the long column certainly show that considerable caution needs to be exercised in the interpretation of chromatograms where reactions are occurring and which can involve several precursors.

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